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Advanced thermo-chemical treatment of waste Bambusa Vulgaris for sustainable resource recovery

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Abstract. Bambusa Vulgaris or Bamboo is one of the rapidly growing woody plants among different species and is not being utilized properly around the world. Hence, the utilization of bamboo for sustainable resource recovery is required to avoid deforestation. This study is focused on thermo-chemical treatment of bamboo waste to investigate the physico-chemical properties of generated products. Experiments were carried out in semi batch, four zone electrically heated, rotary kiln reactor, with reaction time of 90 minutes and heating rate of 25 °C/min, for yield optimization. Products were analyzed through TGA, XRF, SEM/EDS, GCMS and FTIR. From the GCMS study, it was found that the bio-oil obtained through thermo-chemical treatment, contains high amount of alcohols, aldehydes, ketone and phenolic compounds. XRF of biochar showed 11 % inorganic components, among them K and Ca were found to be the major elements. XRF and EDS results were in good agreement and confirmed high carbon content. Biochar had the calorific value of 30.97 MJ/kg, which makes it suitable as energy source for commercial applications. Biochar contained carbonyl (C=O), hydroxyl (HO-), and carboxyl (HOOC) groups, which are responsible for ion exchange reactions during soil amendment. Low ash and high carbon content along with high porosity promotes its usage as high value material in different non-agricultural applications. Additionally, high amount of carbon is beneficial for maximizing the carbon storage and making the process environmentally sustainable.

Introduction

India is in the second position in bamboo cultivation and produces approximately 3.23 milliontons annually. Bamboo is fast growing biomass and it can usually be harvested in 1-4 years. More than 100 species of bamboo are found in Asia [1–3]. Planned harvesting of bamboo cangenerate huge raw material resources for producing value added materials. Other thantraditional applications of bamboo such as furniture manufacturing, building material or medicinal uses, bamboo is being used to produce high value chemicals and biofuels.

Bamboo is made up of hemicellulose, cellulose, and lignin, which are chemically different and have different characteristics. All these components of bamboo plants decompose in different temperature range. Pyrolysis is the process of organic material decomposition under oxygen deprived condition with the application of heat [4,5]. Earlier studies in literature have tried to enhance product yield and optimize the pyrolysis conditions. Depending on the slow or fast pyrolysis and the final use of biochar, the required parameters may be different. The most common use has been as fuel for energy production, heating, and cooking [6].

Higher yield of biochar is obtained through slow pyrolysis in comparison with syngas and bio-oil. Therefore, slow pyrolysis is the adopted technology to produce biochar [7]. Biochar produced from biomass is generally in the range of 20-40 wt % of dry lignocellulose. Pyrolysisconditions such as feedstock, particle size, pressure, holding time, heating rate, and temperature strongly influenced product yield and chemical characteristics of the pyrolysis products [8]. Pyrolysis oil produced from bamboo contain mixture of different chemical compounds such asalcohols, phenols, and acids [9]. During the pyrolysis, micro pores are created which results inlarger microscopic surface area of biochar. Biochar is used for the pollutant removal and nutrients retention in soil, due to its high ion exchange capacity. It contains different functionalgroups which facilitates the ion exchange reactions on the surface of biochar. The transformation of native bamboo by pyrolysis to produce char can be an alternative and potential option for wastewater treatment in the industries, carbon sequestration, oil amelioration and steel making [10].

Zhao et al. showed that during pyrolysis, both operating parameters and feedstock affects the properties of biochar [11]. High lignin content (20 – 40 wt %) makes it an interesting feedstockfor the recovery of aromatic chemicals. [12]. Hernandez-Mena et al. performed slow pyrolysisof bamboo with particle size of 0.7 mm, in fixed bed reactor having 230 mm height and 115 mm of inner diameter. Experiments were performed in the temperature range of 300-600 ºC. Oil yield was 35 wt% along with 25 wt% of biochar and 40 wt% of gases. Oil yield increasedwith increasing temperature but no significant difference in the oil yield was observed beyond500 ºC. Biochar produced from the pyrolysis contained high amount of carbon (up to 80 wt%)and low amount of ash with heating value of approximately 30 MJ/kg [13]. Another bamboo pyrolysis study was carried out by Wang et al. in fixed bed reactor (oven type) in the temperature range of 400-600 ºC with the bamboo particle size of 100 mm. Study revealed thatyield of char decreased with increase in temperature from 46 wt% at 400 ºC to 31 wt% at 600 ºC, and high amount of gases were produced at higher temperature due to secondary cracking.Oil contained mainly levoglucosan, furfurals and aromatics with small quantity of tar. Char produced was highly porous with high carbon content [14].

Most of the previous studies have been carried out using lab scale experimental set-ups [9,15–17]. In this study, pyrolysis of bamboo (Bambusa Vulgaris) was conducted in semi-pilot rotarykiln reactor. Detailed analysis of the bio-oil and char has been carried out for the improved understanding of pyrolysis of bamboo and the quality of the products. Results provided in this study will add necessary information for bamboo pyrolysis for large-scale system developmentand parameter optimization.

Material and Methods

Experimental Procedure:

Bamboo chips were received from local market and the size of bamboo chips were in the rangeof 50 to 120 mm. The thermal behavior of the bamboo was investigated using TGA by heatingin presence of pure nitrogen (100 ml/min) at 20 ºC/min up to 900 ºC. Pure nitrogen was used to remove gaseous condensable products and air in pyrolysis zone. Each experiment in rotary kiln reactor was carried out with 2 kg bamboo chips, that was initially preheated for 1 hr at 150ºC for moisture removal. The experimental set up has been shown in Fig. 1 and details explained in our previous study [18].

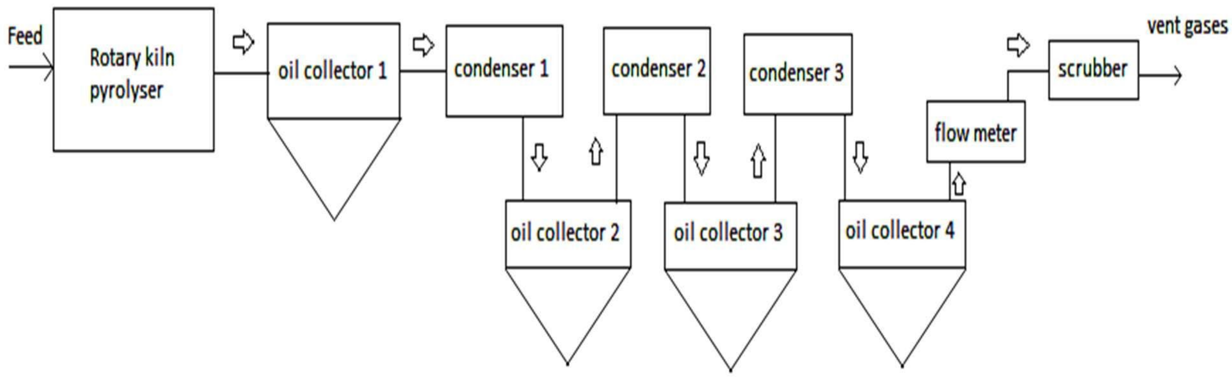

Figure 1: Rotary kiln reactor set-up flow diagram

Characterization Techniques:

The collected oil samples from different biomass feed, at various temperatures were analysed with a Shimadzu-GCMS QP2020 to determine their chemical composition. The GCMS was equipped with a 30 m capillary column. The oven temperature was raised from 50 to 270 ˚C inthe presence of helium with the flow rate of 2 ml/min. For the GCMS analysis of the oil, the method was adopted from the earlier study carried out by Lyu et al. [2015][19].

The feed and product samples were also characterized using various instrumentation techniques such as Scanning Electron Microscope (SEM JEOL make JSM-7610 F-Plus), X-ray fluorescence (XRF) (Epsilon 1 Benchtop Panalytical Germany), Fourier Transform Infrared Spectroscopy (FTIR, Bruker alpha), for detailed analysis. The proximate and ultimate analysiswas carried out using ASTM D7582 and ASTM D3176 standard, respectively. The elemental analysis was carried out using LECO-Truspec CHNS analyser. FTIR was carried out to determine the functional group present in the char. XRF was conducted to determine the elemental composition of solid material and SEM/EDX was carried out for surface topographyand the composition of the pyrolysis char. Products produced at 500 ºC were analysed in this study.

Results and Discussion

Thermal decomposition profile of bamboo was investigated through the thermogravimetric analyser and it was observed that bamboo decomposed in the temperature range of 240 ºC to 700 ºC. At 240-300 °C, the decomposition was mainly due to xylan. Lignin undergoes slow decomposition over a wide temperature range from 300 to 700 °C (Fig. 2). Once the temperature reached close to 400 °C or above, hemicellulose and cellulose decomposed to charand volatiles. Approximately 70 % weight loss occurred between 240 to 600 ºC. Hence, pyrolysis experiments were carried out in the range of 400 to 600 ºC in rotary kiln reactor.

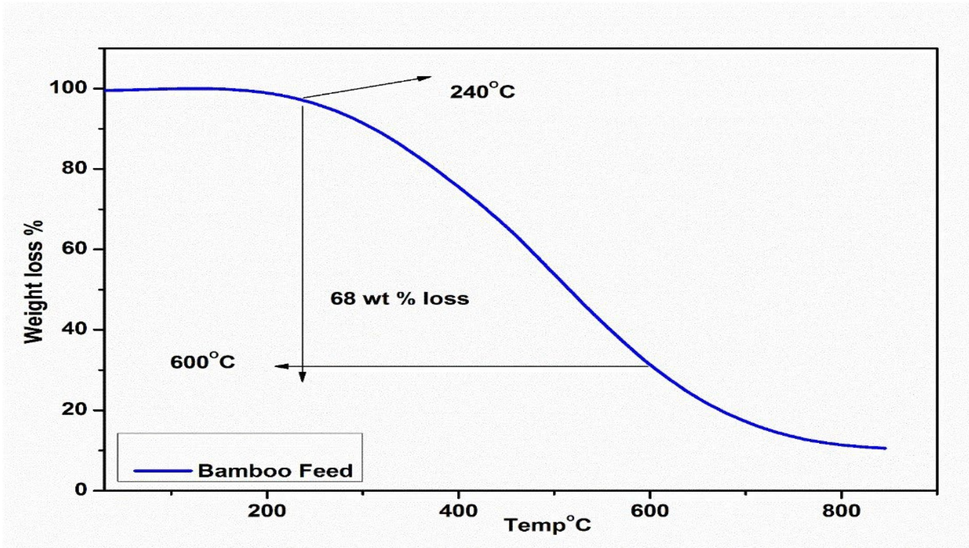

Figure 2: TGA of bamboo feed

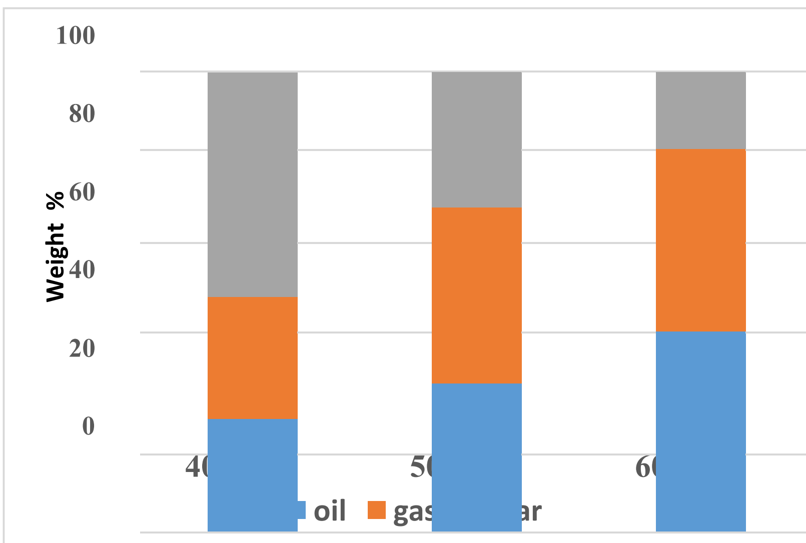

Figure 3: Pyrolysis products yield

As shown in Fig. 3, at temperature around 400 ºC, amount of oil produced was around 25 wt% due to partial decomposition of volatile matters and increased with increase in temperature. As the temperature increased from 500 to 600 ºC, amount of gases increased withno significant change in the oil yield. Higher amount of volatiles were released and the yield of biochar decreased from around 50% to 25% with increase in temperature from 400 to 600 ºC. Results were in well agreement with the previous studies [13-14]. Yield of bio-oil and charcould be increased with optimization of the operating parameters.

Oil Analysis

From the GCMS study, it was found that the bio-oil obtained from bamboo pyrolysis contains alcohols, aldehydes, and ketones with phenolics and aromatic hydrocarbons. Slow pyrolysis also produced high yields of acetic acid. These compounds accounted for 50 area % in total and these compounds are shown in Table 1. Overall, the GCMS data indicated different class of compounds which can be separated from the bio-oil for the recovery of valuable platform chemicals.

Table 1: Bio-oil GCMS analysis

Peak#	R.Time	Area%	Compound Name
1	3.105	2.28	Ethane, 1,1-diethoxy-
2	3.200	10.44	Acetic acid
3	3.753	1.94	2-Propanone, 1-hydroxy-
4	4.348	2.15	2,4-Dimethyl-1-heptene
5	5.572	2.01	Cyclopentanone
6	7.201	2.18	3,5-Dimethylpyrazole-1-methanol
7	8.370	2.92	3-Furanmethanol
8	10.053	1.98	Benzene, 1,2-dichloro-
9	11.379	3.74	Tricyclohex-3-ene-3-carbonitr
10	13.621	4.74	Phenol
11	15.618	3.36	4,4-Dimethyl-cyclohex-2-en-1-ol
12	17.478	2.34	1-Tetradecene
13	21.034	2.48	1-Nonadecene
14	22.405	2.29	,4-Di-tert-butylphenol
15	24.066	2.53	1-Nonadecene
16	26.763	2.38	1-Nonadecene

Char Analysis

X-ray fluorescence spectroscopy

Mineralogical composition of the bamboo char was analysed through XRF. K and Ca were found to be the major micronutrients present in the biochar (Table 2). Overall XRF showed that bamboo char contains low amount of inorganic impurities.

Table 2: XRF analysis of Bamboo char

Compound (wt%)	Sample 1
MgO	0.16
Al O	0.12
SiO_2	1.09
P O	0.173
SO	0.2
K O	6
CaO	2.11
TiO	0.14
Fe O	0.314
Cl	0.65
Loss on ignition	**89**

Ultimate and Proximate Analysis
Char obtained from bamboo contains low amount (4.32 wt %) of moisture. At 500 ºC, the sample contained 77.8 wt % of volatile matter, with high total carbon. It is high in calorific value which makes it suitable as the alternate fuel source (Table 3).

Table 3: Ultimate and Proximate analysis of Bamboo char

Sample ID	Bamboo Char
LOD @ 110 ^{0}C	4.32
Ash @ 800 ^{0}C	13.85
Volatile Matter	77.8
Fix Carbon	4.03
Carbon (%)	78.60
Hydrogen (%)	1.92
Nitrogen (%)	1.823
Sulphur (%)	0.028
Calorific Value MJ/kg	30.97

Scanning electron microscopy-energy dispersive X-ray
Bamboo biochar developed longitudinal pores and high porosity (Fig. 4). Thermal breakdown and large release of volatile matters from bamboo was the reason for the formationof channel like structure. Images showed the surface contains pore size in the range of 2 to 6 µm. It was distinct from the SEM images that biochar prepared at 500 ºC from bamboo also showed honeycomb-like pore structures with defined pores

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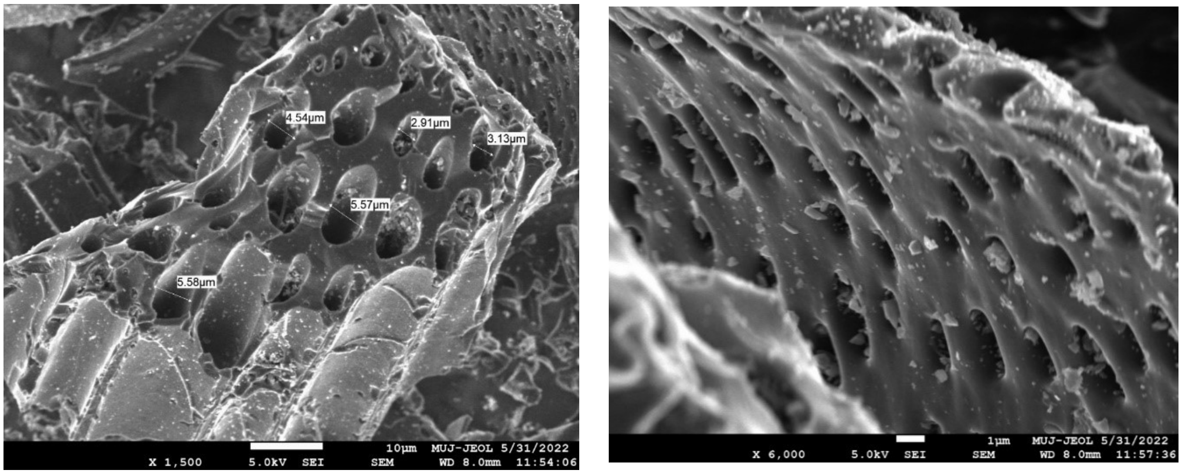

Figure 4: SEM images of Bamboo char

Table 4: Bamboo char EDX analysisFigure 5: EDX graph of bamboo char

Element	Weight %	Atomic %
C	77	85.2
N	0.4	0.4
O	15.7	13
Mg	0.7	0.4
Si	0.4	0.2
K	1.2	0.4

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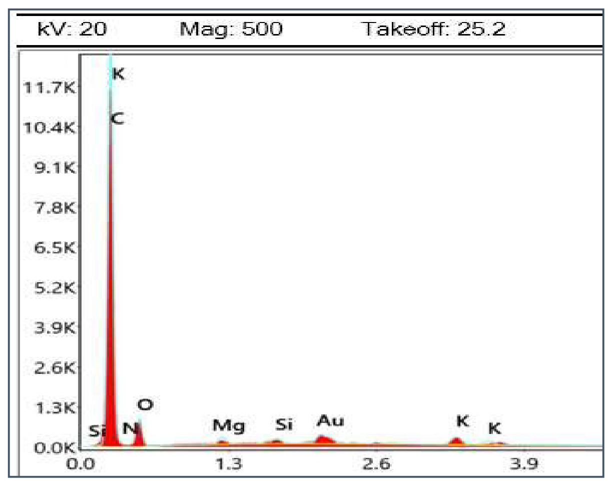

As per Table 4, and Fig. 5, approximately 77 % of char constituted of carbon. The remaining percentage consisted of N, Mg, K and O. These are the essential elements required for soil applications and adsorption process.

Fig. 6 shows that major bands appeared at 875 cm^{-1}, 1517 cm^{-1}, 1697 cm^{-1} and broad range of (3000-3750) cm^{-1}. These peaks correspond to aromatic CH and C-O from carbonates, and C-O vibrations from carbohydrates present in the bamboo feedstock. The peak at around 3750cm^{-1} of O-H groups present in the biochar. Polar functional groups that can enhance bond ability include carbonyl (C=O), carboxyl (HOOC), hydroperoxide (HOO-), and hydroxyl (HO-) groups, were also present.

Fourier transform infrared

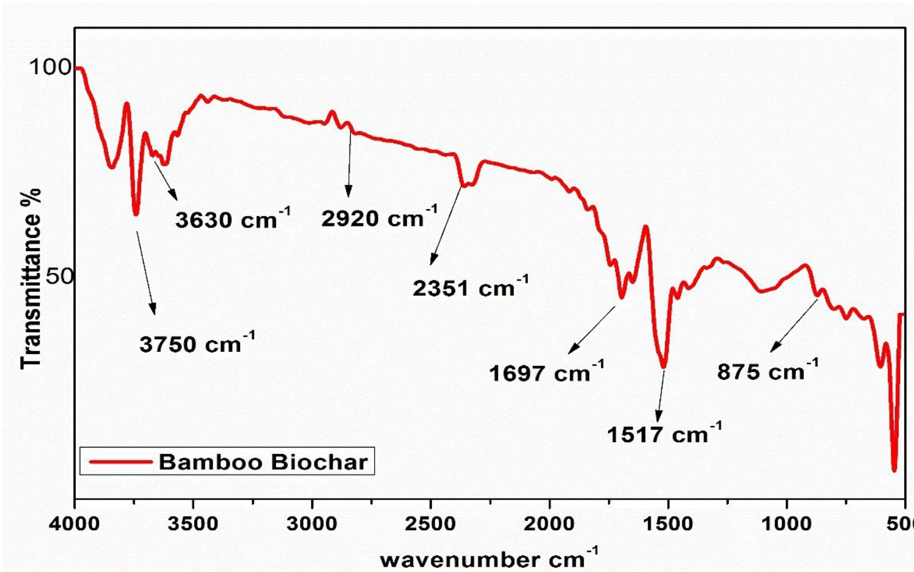

Figure 6: FTIR of Bamboo char

Conclusions

In this research work, thermochemical conversion of bamboo was carried out in temperature range of 400-600ºC using semi-pilot reactor system. Results were in well agreement with the literature studies and revealed information about biochar and bio-oil quality. Study revealed that oil obtained from bamboo contained higher concentrations of acetic acid and phenols, which can be extracted through suitable chemical extraction techniques. Bamboo char has lowash content and high porosity, which render it attractive in many applications. High amount ofcarbon present in biochar is beneficial for maximizing the carbon storage and could be used asenergy source and for soil applications. This also indicates that bamboo has the potential to bea promising precursor to produce activated carbon for different commercial applications.

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